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Polyglycerol- and Sucrose-based Green Polyurethane Adhesives for Veneering

Zelena poliuretanska ljepila za furniranje na bazi poliglicerola i saharoze

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ABSTRACT • Veneering of particleboard with ABS foil and natural oak veneer was performed using polyglycerol- and sucrose-based polyurethane adhesives. Bonding strength between veneer and underlying board was determined according to EN 312 standard. Developed adhesive formulations exhibited bonding strengths between coating material and underlying board exceeding the surface soundness of particleboard (cohesive failure between 50 % and 100 %). Higher adhesion was found for natural oak veneers. Reactivity of the studied adhesives was comparable to those for commercial adhesives used in furniture industry. It has been demonstrated that bio-based polyols can be considered environmentally benign and efficient components of polyurethane adhesives for furniture industry.

Keywords: polyglycerol, polyol, polyurethane, sucrose, veneering

SAŽETAK • Furniranje ploča od usitnjenog drva ABS folijama i hrastovim furnirom provedeno je uz primjenu poliuretanskih ljepila na bazi poliglicerola i saharoze. Čvrstoća lijepljenja furnira na ploču određena je prema normi EN 312. Razvijenim formulacijama ljepila postignute su veće čvrstoće lijepljenja između prevlake i ploče nego što je međuslojna čvrstoća ploče od usitnjenog drva (kohezijski lom između 50 i 100 %). Veća adhezija zabilježena je na hrastovim furnirima. Reaktivnost ispitivanih ljepila bila je usporediva s komercijalnim ljepilima koja se upotrebljavaju u industriji namještaja. Utvrđeno je da se polioli na prirodnoj bazi mogu smatrati ekološki prihvatljivim komponentama poliuretanskih ljepila za industriju namještaja.

Ključne riječi: poliglicerol, polioli, poliuretan, saharoza, furniranje

1 INTRODUCTION

1. UVOD

Nowadays, the principles of green chemistry and concept of sustainable development impose research and industrial implementation of the materials derived from renewable feedstock. Bioplastics or bio-based polymers seem to be the solutions of tomorrow, so that novel materials employing renewable resources are considered to be alternatives for oil-derived raw materials (Mamiński and Toczyłowska-Mamińska, 2017).

Technology of today and modern industrial operations are expected to comply with the principles of green chemistry, so that the impact on environment has been reduced. Increasing demand on greener products results in the development of renewable feedstock-based materials, including adhesives, wherever technically feasible.

These days intense development of furniture industry is observed. In Poland only market value reached 9.5 bln euro in 2016 and is expected to reach 11.1 bln euro in 2020 (KMPG, 2017). Furniture is mostly made of veneered wood-based panels like par-

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tleboard and fiberboard. Thus, due to high volume of the materials used in veneering, they have substantial impact on the environment. One of the approaches to increase environmental friendliness of furniture production is asymmetrical veneering that was described for the first time long time ago by Hayward (1949). When properly implemented, it results in the reduction of production costs and reduced demand for wood of valuable species. It was demonstrated in the literature that mechanical and physico-chemical properties of the substrates subjected to adhesive bonding strongly affected the tendency of the 'veneer-adhesive-board' system to deformations (Oleńska *et al.*, 2014; Král *et al.*, 2013). It has been confirmed that the type of the adhesive has an effect on product durability and stability of its shape. As previously shown, polyurethanes combine excellent adhesive properties with elasticity providing reduced deflection in veneered materials (Mamiński *et al.*, 2011; Oleńska *et al.*, 2014). Therefore, a research on novel types of environmentally friendly adhesives is fully justified.

Glycerol is an environmental-friendly resource that can be readily transformed into a number of chemicals including polymers. One of the pathways is conversion of glycerol into polyglycerols (Rokicki *et al.*, 2005). Hyperbranched polyglycerols have been shown to be effective components of polyurethane (PUR) adhesives for wood bonding (Mamiński *et al.*, 2011; Mamiński *et al.*, 2012).

Sucrose is another cheap, easily available and renewable resource that can be conveniently converted into a variety of semi-products for industrial applications – including sucrose-based polyols for PUR (Ionescu and Petrović, 2010).

The present study deals with the use of sucrose-based and polyglycerol-based polyols in polyurethane adhesives to replace petroleum-derived ones. Typical areas of use of the sucrose-based polyols are insulating foams, elastomers and thermoplastic polyurethanes. Neither former nor latter have ever been used solely as polyol components in PUR adhesives for veneering. Thus, the aim of the present study is to maximize the content of polyols derived from renewable resources in the adhesives dedicated to furniture industry. Therefore, the investigated polyols were not used in mixtures with other types of polyhydroxyl compounds. The PUR adhesives were examined as binders in particleboard veneering for furniture manufacturing. The practical applicability of the sucrose- and polyglycerol-based polyols in polyurethane formulation has been demonstrated and, thus, they may be considered significant green resources in the future.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

Two types of coating materials were employed in experiments: 0.6 mm thick oak veneer and 0.4 mm thick decorative ABS veneer.

Three green polyols were used in the study: a hyperbranched polyglycerol (A) and two commercially

available propoxylated sucrose polyols C (yellow liquid, viscosity 7050 mPa·s at 20 °C, hydroxyl number 425 mg KOH/g, hydroxyl functionality 5) and J (transparent liquid, viscosity 6360 mPa·s at 25 °C, 422 mg KOH/g, hydroxyl functionality 4.5) both manufactured by Oltchim (Romania).

Polyglycerol A was synthesized according to the procedure described by Rokicki *et al.* (2005) from glycerol carbonate (4-hydroxymethyl-1,3-dioxolane-2-on) and 1,1,1-tris(hydroxymethyl)-propane (10/1, mol/mol). The product was a brown liquid of viscosity of 9100 mPa·s at 20 °C, hydroxyl number 735 mg KOH/g and hydroxyl functionality 13. Polymeric methylenediphenyldiisocyanate (PMDI, NCO content 36 %) manufactured by (Huntsman Co., USA) was used as obtained.

2.1 Adhesive preparation

2.1. Priprema ljepila

The amount of PMDI in PUR was calculated using the formula (1) (Monument Chemical, 2014), in which polyol amount and hydroxyl number are taken into account. NCO index is a molar NCO/OH ratio. When the number of NCO groups equals the number of OH groups, NCO index is 1.0. If more than one polyol is used in a formulation, the sum of weights multiplied by hydroxyl numbers are placed in the numerator in Eq. 1.

$$m_{iso} = \left(\frac{\sum m_{polyol} \times L_{OH}}{56100} \right) \cdot \frac{4202}{c_{iso}} \quad (1)$$

Where:

m_{iso} – stoichiometric amount of isocyanate for NCO index 1.0 (g),

m_{polyol} – amount of polyol (g),

L_{OH} – polyol hydroxyl number (mg KOH/g),

c_{iso} – NCO content in PMDI (%wt).

Target NCO index was 1.0. Weighted amounts of the polyol and isocyanate components were mixed in a plastic cup for 5 seconds using a high-speed mixer. Tin octanoate Sn(Oct)₂ was used as catalyst (0.05 %wt).

2.2 Veneering

2.2. Furniranje

The adhesive was applied on the substrate (300 mm × 300 mm × 16 mm particleboard) in the quantity of 200 g/m², and then veneer was placed onto the adhesive and pressed (60 °C, 1.0 MPa, 4 minutes). Specimens were conditioned at (20±2) °C and (65±5) % relative humidity for 7 days before testing.

2.2 Pull-off test

2.2. Pull-off ispitivanje

The strength of bonding between the coating material and the underlying board was determined from the pull-off test performed according to the European standard EN 311 24 hours after bonding steel pad with hot-melt adhesive onto the surface. The Eq. (2) was used to calculate the bondline strength (R).

$$R = \frac{F_{max}}{S} \quad (2)$$

Where:

F_{max} – maximum force (N),

S – surface area (mm²).

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 PUR reactivity

3.1. Reaktivnost poliuretanskog ljepila

The polyurethane chemistry is mainly based on the reaction of an isocyanate group (NCO) with compounds with active hydrogen atoms, i.e. hydroxy and amine groups, and water. The relative reactivity of the isocyanate group (NCO) toward hydroxyls varies substantially. According to Lay and Cranley (1994) under conditions without a catalyst, the relative reaction rates for primary hydroxyl groups is about 100, while that for secondary hydroxyl groups is about 30. However, the use of appropriately selected catalysts can radically change these values, as well as the order of reactivity (Britain and Gemeinhardt, 1960). It is commonly agreed that chemical structure and hydroxyl functionality of the polyol also have a strong effect on such adhesive properties like gelling time and mechanical properties of bondline. On the other hand, strength of a polymer is determined by the stiffness, hardness and density of crosslinking (Suo, 1990). That is why the chemical structure of a polyol is an important parameter that affects polyurethane gelling time and its mechanical properties.

The basic properties of PURs used in the study are shown in Table 1. The polyols C and J may seem much alike and close in characteristics; however, slightly different OH functionality (5 vs 4.5, respectively, for C and J) was expected to yield different behavior. It is reported in the literature that physical and mechanical properties of polyurethane materials are

largely associated with cross-linking density (Dong *et al.*, 2011; Maji and Bhowmick, 2009). The results indicate that reactivity of the PURs is adequate for industrial processing and the adhesives systems are suitable for veneering. What is more important, the gelling time will be markedly shortened under true industrial process, where applied temperature is much above ambient and usually ranging between 60 °C and 150 °C depending on the adhesive. The gelling tests performed at 80 °C revealed that the catalyzed adhesive I gelled in just 45 seconds. Thus, it is clear that short, industrially practical pressing times can be obtained after proper tuning of PUR formulations. Data in Table 1 indicate the effect of hydroxyl functionality on the gelling time of the formulations. The adhesive containing 13-functional polyglycerol A exhibited higher reactivity at 20 °C when compared to 5- and 4.5-functional sucrose-based polyols C and J. The phenomenon confirms the influence of hydroxyl groups abundance on curing rate and network formation in PUR (Sonnenschein and Wendt, 2005).

3.2 Veneering and pull-off test

3.2. Furniranje i pull-off ispitivanje

In order to shorten pressing time, initial veneering was performed at 87 °C; however, due to too high temperature and plasticizing of the ABS, foil bubble forming occurred (Figure 1) which is an apparent and unacceptable defect in veneering. The phenomenon did not occur for natural oak veneers. Lowering the temperature to 60 °C improved the veneering quality, so that flat, smooth and non-defective surface was produced.

Table 1 Formulations and gelling times of the investigated PURs

Tablica 1. Formulacije i vrijeme želiranja istraživanih poliuretanskih ljepila

| Adhesive <i>Ljepilo</i> | Polyol <i>Poliol</i> | Isocyanate <i>Izocijanat</i> | NCO index <i>NCO indeks</i> | Gelling time at 20 °C, min / <i>Vrijeme želiranja pri 20 °C, min</i> | |
|----------------------------|-------------------------|---------------------------------|--------------------------------|--|--------------------------------------|
| | | | | Catalyzed / <i>Kataliziran</i> | Non-catalyzed / <i>Nekataliziran</i> |
| I | A | PMDI | 1.0 | 8.5 | 50 |
| II | C | PMDI | 1.0 | 10 | > 60 |
| III | J | PMDI | 1.0 | 10 | > 60 |

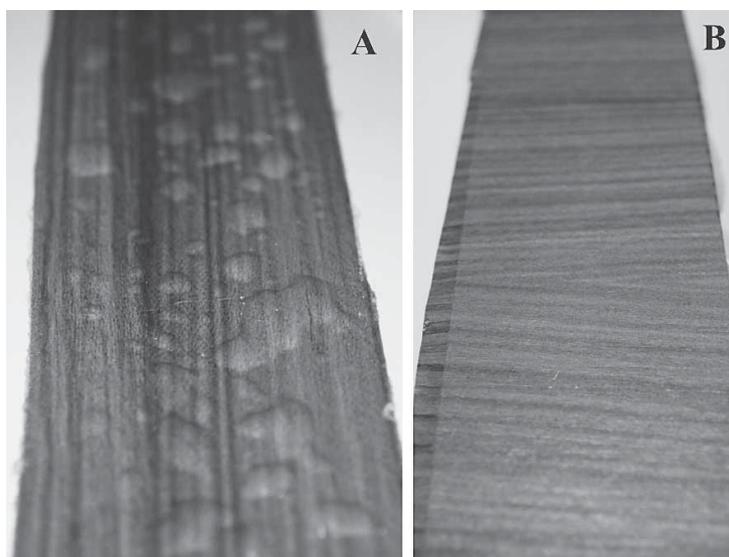


Figure 1 A – bubble forming under ABS foil (pressing at 87 °C) and B – avoided bubbling (pressing at 60 °C)
Slika 1. A – stvaranje mjehura ispod ABS folije (prešanje pri 87 °C), B – folija bez mjehuranja (prešanje pri 60 °C)

Table 2 Results of bonding strength determined according EN 311**Tablica 2.** Rezultati čvrstoće lijepljenja određene prema EN 311

| Adhesive <i>Ljepilo</i> | Veneer <i>Furnir</i> | R | Cohesive failure in particleboard <i>Kohezijski lom u ploči od usitnjenog drva</i> |
|----------------------------|-------------------------|------------|---|
| | | MPa | % |
| I | ABS | 0.21±0.08 | 0 |
| | Oak / <i>hrast</i> | 0.23 ±0.05 | 0 |
| II | ABS | 0.51±0.12 | 50 |
| | Oak / <i>hrast</i> | 0.31±0.10 | 0 |
| III | ABS | 0.41±0.11 | 80 |
| | Oak / <i>hrast</i> | 0.44±0.10 | 100 |

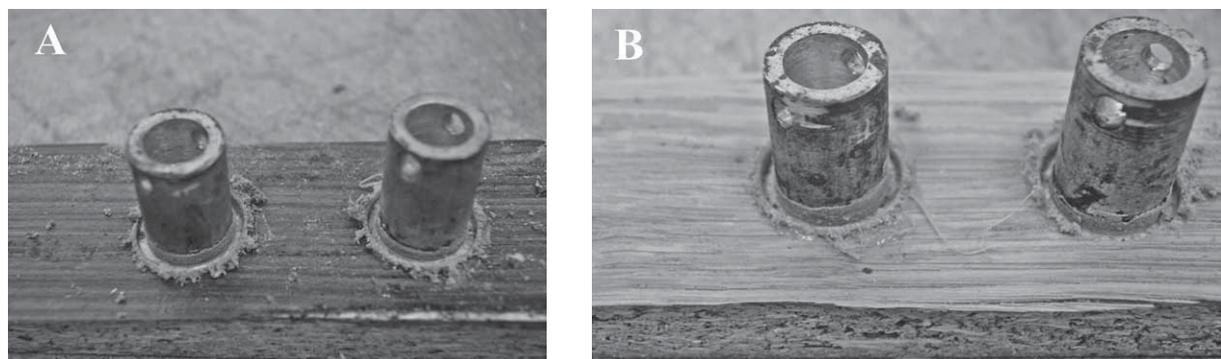
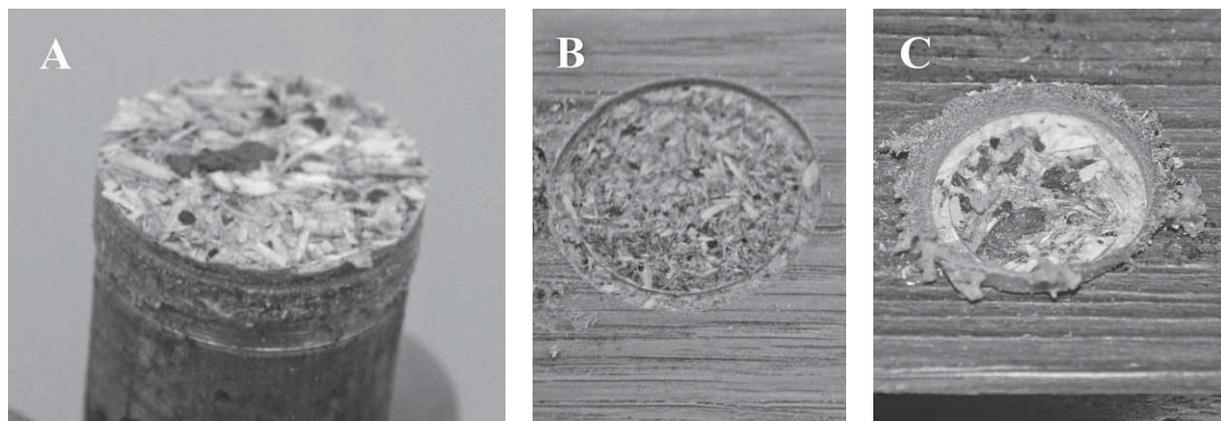
Subsequently, specimens for pull-off tests were veneered at 60 °C (Figure 2). The results of determination of bonding strength in veneer-particleboard system are shown in Table 2. It can be seen that the adhesive I yielded the lowest bondline strengths and neither for ABS nor for oak veneer cohesive failure occurred. Thus, it is apparent that polyglycerol-polyol provided poor mechanical performance, which can be associated with high cross-link density in polymer due to hydroxyl functionality as high as 13. It has been reported in the literature that too high cross-linking results in lowered mechanical performance of PUR (Dong *et al.*, 2011; Maji and Bhowmick, 2009).

On the other hand, adhesives II and III, both based on sucrose-polyols, rendered higher strengths. The observed *R* values ranged between 0.31 MPa and 0.51 MPa, while cohesive failure rates varied from 50 % to 100 % (Figure 3). Such low surface soundness of

particleboard was surprising as the minimum requirement for commercial particleboard defined in EN 312 is 0.8 MPa. However, apparently the adhesives II and III are comparable in terms of veneer bonding quality, and adhesion to ABS and oak veneers is probably similar.

Hence, it is clear that, contrary to initial expectations, hydroxyl functionality of C and J polyols (5 and 4.5, respectively) had no effect on mechanical performance of bondlines.

The findings discussed above indicate that glycerol- and sucrose-based polyols can be considered perspective components of PUR adhesives; however, there is still a need for proper formulation of adhesives. When properly formulated, polyurethanes based on PMDI and green polyols, derived from renewable glycerol and sucrose, can be potentially used as binders in veneering at industrial scale

**Figure 2** Specimens prepared for pull-off test: A – ABS veneer, B – oak veneer**Slika 2.** Uzorci pripremljeni za *pull-off* ispitivanje: A – ABS, B – hrastov furnir**Figure 3** Pull-off tests: cohesive failure in particleboard: A – steel pad, B – oak veneer, C – ABS veneer**Slika 3.** *Pull-off* ispitivanje: kohezijski lom u ploči od usitnjenog drva: A – čelični čepić, B – hrastov furnir, C – ABS

4 CONCLUSIONS

4. ZAKLJUČAK

It was demonstrated that the proposed PUR formulations exhibited practically useful reactivity as well as satisfactory strengths of bonding between coating material and underlying board. Therefore, it can be concluded that polyglycerol- and sucrose-based biopolyols are environmentally-benign, efficient and prospective components of polyurethane adhesives that may substitute petroleum-based polyols in furniture industry.

Further research should be focused on optimization of veneering conditions (temperature, pressure, time), so as to minimize the occurrence of defects (e.g. bubbles).

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5 REFERENCES

5. LITERATURA

1. Britain, J. W.; Gemeinhardt, P. G., 1960: Catalysis of the isocyanate-hydroxyl reaction. *Journal of Applied Polymer Science*, 4: 207-211. <http://dx.doi.org/10.1002/app.1960.070041112>.
2. Dong, L.; Liu, B.; Xu, L.; Budziński, K. L.; Shou C., 2011: Synthesis of hyperbranched polyester-amides and their application as crosslinkers for polyurethane curing systems. *Journal of Applied Polymer Science*, 121: 957-963. <http://dx.doi.org/10.1002/app.33678>.
3. Hayward, C., 1949: *Practical veneering*. Bell & Hyman, London.
4. Ionescu, M.; Petrović, Z. S., 2010: High Functionality Polyether Polyols Based on Polyglycerol. *Journal of Cellular Plastics*, 46: 223-237. <http://dx.doi.org/10.1177/0021955X09355887>.
5. Lay, D. G.; Cranley, P., 1994: *Polyurethane adhesives*. Pizzi, A. and Mittal, K. L. (eds.). *Handbook of adhesive technology*. Marcel Dekker, New York.
6. Král, P.; Hrázský, J.; Hrapková, L.; Hamšík, P., 2013: Shape Stability of Particleboards Covered with Decorative Veneers. *Drvna industrija*, 64: 211-220. <http://dx.doi.org/10.5552/drind.2013.1234>.
7. Maji, K. P.; Bhowmick, A. K., 2009: Influence of number of functional groups of hyperbranched polyol on cure kinetics and physical properties of polyurethanes. *Journal of Polymer Science, Part A: Polymer Chemistry*, 47: 731-745. <http://dx.doi.org/10.1002/pola.23185>.
8. Mamiński, M.; Parzuchowski, P.; Trojanowska, A.; Dziejewski, Sz., 2011: Fast-curing polyurethane adhesives derived from environmentally friendly hyperbranched polyglycerols – the effect of macromonomer structure. *Biomass and Bioenergy*, 35: 4461-4468. <http://dx.doi.org/10.1016/j.biombioe.2011.09.012>.
9. Mamiński, M. Ł.; Szymański, R.; Parzuchowski, P.; Antezak, A.; Szymona, K., 2012: Hyperbranched polyglycerols with bisphenol A core as glycerol-derived components of polyurethane wood adhesives. *BioResources*, 7: 1440-1451. <http://dx.doi.org/10.15376/biores.7.2.1440-1451>.
10. Mamiński, M. Ł.; Toczyłowska-Mamińska, R., 2017: Bio-derived adhesives and matrix polymers for composites. Thakur, V. K.; Thakur, M. K.; Kessler, M. R. (eds.). *Handbook of composites from renewable materials*, Vol. 1: *Structure and Chemistry* Wiley-Scrivener, pp. 151-188. <http://dx.doi.org/10.1002/9781119441632.ch7>.
11. Oleńska, S.; Tarcicki, P.; Mamiński, M.; Beer P., 2014: Effectiveness of asymmetrical veneering with hardwood species of varying shrinkage and porosity. *Drvna industrija*, 65: 139-142. <http://dx.doi.org/10.5552/drind.2014.1315>.
12. Rokicki, G.; Rakoczy, P.; Parzuchowski, P.; Sobiecki, M., 2005: Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate. *Green Chemistry*, 7: 529-539. <http://dx.doi.org/10.1039/b501597a>.
13. Sonnenschein, M. F.; Wendt, B. L., 2005: Efficacy of polymeric MDI/Polyol mixtures for binding wood boards. *Wood Science and Technology*, 39: 27-36. <http://dx.doi.org/10.1007/s00226-004-0266-0>.
14. Suo, Z., 1990: Failure of brittle adhesive joint. *Applied Mechanics Reviews*, 43: 276-279. <http://dx.doi.org/10.1115/1.3120827>.
15. ***EN 311: 2002 Wood-based panels – Surface soundness – Test metod.
16. ***EN 312: 2004 Particleboards – Specifications.
17. ***Monument Chemical Kentucky LCC, Terms and formulas used in urethane polymer preparations, July 2014 http://www.pmahome.org/files/5314/1460/1437/Urethane_terms_NEW.pdf. (Accessed June 20, 2018).
18. ***KMPG, Rynek meblarski w Polsce – raport (in Polish), June 2017. <https://assets.kpmg.com/content/dam/kpmg/pl/pdf/2017/06/pl-Raport-KPMG-Rynek-meblarski-w-Polsce-2017.pdf>. (Accessed June 21, 2018).

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